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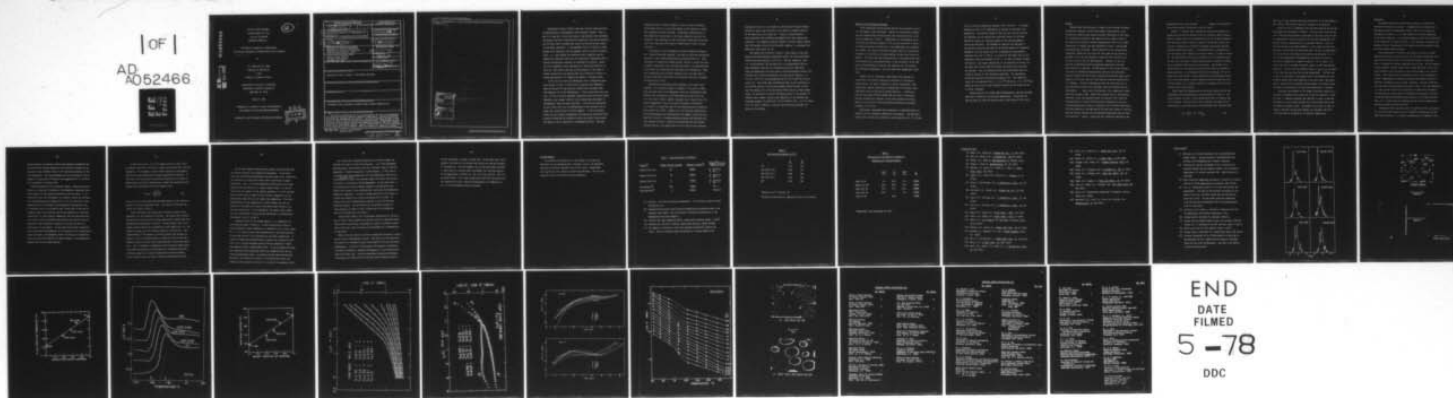   MAR 78   R E COHEN, A R RAMOS   N00014-77-C-0311
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Viscoelastic Properties of Homopolymers

and Diblock Copolymers of Polybutadiene and Polyisoprene

by

R.E. Cohen and A.R. Ramos

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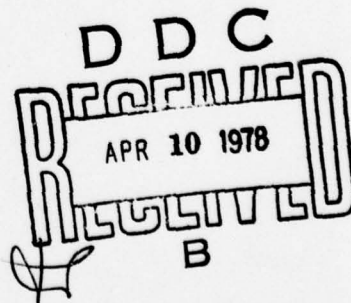Advances in Chemistry Series

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Three diblock copolymers of cis-1,4 polyisoprene (IR) and 1,4 polybutadiene (BR) have been studied in dynamic mechanical experiments, transmission electron microscopy and thermomechanical analysis. The block copolymers had molar ratios of 1/2, 1/1 and 2/1 for the isoprene and butadiene blocks. Homopolymers of polybutadiene and polyisoprene with various diene microstructures were also examined using similar experimental methods. Results indicate that in all three copolymers the polybutadiene and polyisoprene blocks are essentially compatible, whereas

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blends of homopolymers of similar molecular weights and microstructures were incompatible.

Considerable research efforts have been directed towards gaining an understanding of heterogeneous block copolymer systems. This is due in a large part to the wide range of such materials now available, the unusual and often unique physical properties which may be obtained, and the wide range of morphologies which can form during the process of microphase separation. A corresponding level of interest in homogeneous block copolymers has not emerged, owing to similar considerations - i.e. such systems are relatively rare, properties are not dramatically different from those of conventional homopolymers and no distinct morphological features are available for analysis. Nevertheless, homogeneous block copolymers are interesting materials in their own right because they may provide guidance in the study of polymer compatibility and because they are of potential interest as morphology-regulators or "homogenizing agents" in polymer blends.

In the rare case that two homopolymers form a homogeneous molecular mixture in bulk, it would also be expected that homogeneity would be observed in high molecular weight block copolymers made from sequences of the two homopolymers. A more interesting case, however, is that of a block copolymer system which does not exhibit phase separation even though a blend of the corresponding homopolymers is heterogeneous under the same conditions. A qualitative explanation of this latter case lies in considerations of the covalent link between each successive pair of block segments. If the constituent blocks are not strongly incompatible, the constraint provided by this covalent linkage may be sufficent to force the overall block copolymer material into a compatible or semicompatible state. The semi-

compatible state (1) may be viewed as a case in which interfacial mixing takes place to a sufficient degree so that regions of either pure component are never achieved. Experimental determination of the composition fluctuations in this semi-compatible state will be hindered by the gentleness of the fluctuations themselves and by the small size range over which they are constrained to occur in block copolymers.

Few examples of the "homogeneous diblock-incompatible homopolymer" behavior have been reported. One that has received considerable attention is the system polystyrene-polyα-methylstyrene (2). Block copolymers of styrene and α-methylstyrene exhibit a single loss peak in dynamic experiments (2,3) and have been shown to be thermorheologically simple (4); hence they are considered to be homogeneous. Mechanical properties data on these copolymers have also been used to validate interesting extensions of the molecular theories of polymer viscoelasticity (2,3,4).

Polycarbonate-polysulfone block copolymers with rather short segments, i.e., molecular weight of segments in the order of 5000, have also been found to be homogeneous while the corresponding homopolymers are incompatible at the same molecular weight level (5). It is not clear, however, whether copolymers with longer blocks will also be homogeneous since the solubility parameter differential ($\sim$1.4 J/cm^3) is larger than that of the polystyrene-polyα-methylstyrene system ($\sim$0.4 J/cm^3). Angelo et al. (6) observed compatibility of the polybutadiene and polyisoprene block segments (both with less than 10% 1,4 units) in styrene-butadiene-isoprene and butadiene-styrene-isoprene triblocks. Blends of styrene-butadiene and styrene-isoprene diblocks also showed some mixing of the two diene segments,

although mixing was not as complete as that obtained through terpoly-
merization, where some indication of the effect of segment position
on the blending was also noted (6). Finally, styrene-butadiene
block copolymers have exhibited semicompatibility under appropriate
conditions. Low segmental molecular weights (7) and/or higher tempera-
tures (8) promote mixing of the dissimilar segments, in agreement with
theoretical predictions (9, 10).

The present work considers in detail a new example of the homo-
geneous block-heterogeneous homopolymer system, for which preliminary
results have been reported (1,11,12,13). The two components, high
cis 1,4 polyisoprene (IR) and medium cis 1,4 polybutadiene (BR) are
both elastomeric materials of considerable practical importance.
These two hompolymers have been found to form heterogeneous blends (14),
although their solubility parameters are very nearly identical, i.e.
17.0-17.2 J/cm^3 for the polybutadiene and 16.4-16.8 J/cm^3 for polyiso-
prene (15). The system under consideration here may be considered to
be the diene analog of the styrene-α-methyl styrene system; in each
case the repeat units of the two blocks differ only by a single methyl
group. An additional structural difference arises in the polymers of
interest here, however, owing to the capability of the isoprene and
butadiene monomers to polymerize in four different ways - cis 1,4; trans
1,4; 1,2; and 3,4 addition - with the last two being equivalent for
the case of butadiene.

Materials and Experimental Methods

Three polybutadiene/polyisoprene diblocks were provided to us by Dr. Paul Rempp of CRM, Strasbourg. Details of the molecular weights and the expected diene microstructures were discussed earlier (1,13) and are summarized in Table 1. Homopolymers of corresponding micro-structures and molecular weights (1,13) are also described in Table 1. The molecular weight distributions of the homopolymers are considera-bly broader than those of the block polymers owing to a mastication procedure (13) carried out on these samples to lower their molecular weights. To insure that the microstructures of the homopolymers were well matched to the constituent blocks in the copolymers, 60 MHz NMR spectra were obtained on a Varian T-60 apparatus for the diblocks, the individual homopolymers, and three equivalent homopolymer blends (13).

Samples for the viscoelastic experiments were prepared by a conventional slow solvent evaporation technique (1) followed by vacuum drying. For ease in handling in certain experiments, some samples were lightly cured using a 30 MRad dose of electrons; other experiments were carried out on uncured materials. Trnasmission electron microscopy (Phillips Model 200) was used to investigate possible morphological features in the block polymers and blends. Details of the various staining techniques employed are presented elsewhere (1,11,12,13).

Viscoelastic experiments were conducted on a Rheovibron DDV-II-C apparatus and on a Rheometrics Mechanical Spectrometer. The Rheovibron studies were carried out in tension on cured samples at 3.5, 11, 35 and

110 Hz at various temperatures between -135° C and 40° C. A nitrogen blanket was used at all temperatures to protect the specimens from degradation. The end-butt method of Voet (16) was used for gripping the specimens and the appropriate correction factors (17,18) were applied to account for required changes in the specimen geometry during the experiment. The Rheometrics apparatus was employed in the eccentric rotating disk mode (8) on uncured samples at frequencies between 0.1 and 100 rad/sec and over a temperature range generally extending from -40° C to 40° C; in a few cases the upper limit of the temperature range was extended to 175° C. In order to obtain reliable information in the sample temperature, it was necessary to shield (13) the upper test fixture from the nitrogen gas stream used to blanket the specimen. Also, all measured forces and displacements were corrected to account for the instrument compliance. The appropriate correction equations are presented elsewhere (13). The compliance values for our apparatus are K_x = 3.2 x 10^{-6} m/N and K_y = 2.7 x 10^{-6} m/N; these are close to the values reported by Gouinlock and Porter (8) for a similar instrument.

Thermal analysis on a DuPont 900 thermomechanical analyzer provided additional information on transition temperatures. A blunt-end expansion probe was used with heating rates in the range of 5-10° C/min.

Results

Because diene microstructure is known to have a marked influence on physical properties, we felt that proper interpretation of our viscoelastic studies would require detailed information of this type. The information provided by the suppliers of our samples (Table 1) was based on the method of anionic polymerization used in the sample preparation; to support the data presented in Table 1, various NMR experiments were performed. Results obtained on the polybutadiene homopolymer showed that less than 10% vinyl addition was present as expected, but it was not possible to determine the cis/trans ratio for the 1,4 units with our NMR apparatus. Likewise, it was only possible to demonstrate that polyisoprene homopolymer contained more than 92% 1,4 addition. The NMR spectra of the various diblocks could not be interpreted quantitatively owing to the complicated overlap of peaks from the various isoprene and butadiene repeat units; however, it was clear that all three samples contained predominantly 1,4 linkages. In order to demonstrate that the microstructures of the constituent blocks of our copolymers were well matched with the homopolymers used in our investigation, three homopolymer blends were also studied in NMR. Blend 2144 contained 39 wt % polyisoprene, identical to the polyisoprene content of copolymer 2144; similarly the compositions of blends 2143 and 2148 corresponded to the poly-isoprene/polybutadiene ratios of copolymers 2143 and 2148 respectively. The close matching of the NMR spectra for each pair (Figure 1) confirms that the diblock segments and corresponding homopolymer have the same microstructure. Figure 1, along with the information obtained on the

homopolymers alone, also provides   support of the quantita-
tive microstructural information listed in Table 1.

Figure 2 presents some transmission electron micrographs ob-
tained using the ebonite method (13,19) for obtaining phase contrast.
Figure 2a shows clearly the incompatibility of the IR and BR homopoly-
mers and also provides a typical example of the degree to which the
staining technique can differentiate between polyisoprene and poly-
butadiene phases when present. A high magnification micrograph of a
pure IR sample, also treated by the ebonite method, is shown in Figure
2b. No morphological features are evident in this micrograph except
for the "salt and pepper" texture characteristic of nearly all materi-
als at very high resolution on our microscope. Micrographs of all
three diblocks at low and medium magnification showed no evidence of
phase separation. At high magnifications the micrographs of the di-
blocks were very similar to those obtained on the homopolymers except
for a few diffuse darker regions randomly scattered around the field
of view; Figure lc is a typical example for copolymer 2143 (1/1) con-
taining 56 wt % polyisoprene.

Glass transition temperatures of the three diblocks and the two
homopolymers are plotted against isoprene content in Figure 3. The
values plotted in Figure 3 were determined by TMA at a heating rate
of 5° C/minute. The points fall near a straight line which can be
described by a simplified version of the Gordon-Taylor equation (20):

$$T_g = W_I T_{gI} + (1 - W_I)T_{g_B} \qquad (1)$$

where T_{gI} and T_{gB} represent the glass transitions of the two homopolymers and W_I is the weight fraction of isoprene in the material.

Curves of tanδ vs. temperature for the three diblocks and the two homopolymers are presented in Figure 4. The two arrows along the abscissa indicate the positions of the peaks in the tanδ curves for the two homopolymers; the peak locations for the three homopolymers fall between these two temperatures in a systematic fashion. Also, we note the absence of any peak broadening in the curves for the block copolymers, indicating that the single peak for each of these materials is not due to the merging of two poorly resolved peaks (1). A plot of the temperature corresponding to the maximum in tanδ as a function of composition is shown in Figure 5. As in Figure 3, all points fall near a straight line which, again, is well described by Equation 1; in this case the limiting values of T_{gB} and T_{gI} are taken as the tanδ peak locations for the two homopolymers. The fact that values of T_g obtained in the dynamic mode on the Rheovibron are all slightly greater than those obtained in the quasi-static TMA experiment is qualitatively consistent with well-known rate effects which influence all measurements of transition temperatures in polymers.

Isothermal measurements of the dynamic mechanical behavior as a function of frequency were carried out on the five materials listed in Table 1. Numerous isotherms were obtained in order to describe the behavior in the rubbery plateau and in the terminal zone of the viscoelastic response curves. An example of such data is shown in Figure 6 where the storage shear modulus for copolymer 2148 (1/2) is plotted against frequency at 10 different temperatures.

Discussion

The method employed to provide phase contrast in transmission electron microscopy was successful in demonstrating the presence of a two-phase structure in homopolymer blends of BR and IR (Figure 2a). The opposite situation, i.e. a clear absence of any phase separation in the block copolymers, is also demonstrated, but much less convincingly by the comparison of Figure 2b and 2c. It is necessary to consider the evidence from all the mechanical and thermal analysis experiments along with the evidence from microscopy.

Close examination of Figure 2c and others of similar or higher magnification does not reveal any hint of the regular morphology, with characteristic domain sizes in the range of hundreds of angstroms, which is expected for diblock copolymers of this type. We did freqently observe, however, diffuse darker regions about 200-400 Å in size scattered randomly around the field of view in micrographs of all the diblocks. These regions were not observed in any of the micrographs of stained homopolymers and therefore cannot be attributed directly to artifacts introduced by the staining technique. Instead, we believe that the three block copolymers described in Table 1 are "semicompatible", i.e. they contain significant fluctuations in composition throughout the bulk material; these gentle fluctuations do not appear to be part of any well-organized morphology and, based on all the data obtained here, it is unlikely that the fluctuations ever lead to regions which consist of either pure BR or pure IR.

The Gordon-Taylor Equation, which in simplified form was successful in fitting data (Figures 3-5) on transition temperatures for the BR/IR block copolymers, is based on considerations of segmental inter-

action energies; the equation carries the underlying assumption that the interactions between segments of the dissimilar polymers can be expressed as the arithmetic mean of the interaction energies for the two homopolymers. The close agreement with our experimental results suggests a large degree of mixing at the segmental level in the three block copolymers of interest here.

Detailed analysis of the isothermal dynamic mechanical data obtained as a function of frequency on the Rheometrics apparatus lends strong support to the tentative conclusions outlined above. It is important to note that heterophase (21) polymer systems are now known to be thermorheologically complex (22, 23, 24, 25) resulting in the inapplicability of traditional time-temperature superposition (26) to isothermal sets of viscoelastic data; limitations on the time or frequency range of the data may lead to the appearance of successful superposition in some ranges of temperature (25) but the approximate shift factors (26) thus obtained show clearly the transfer from the dominance of the viscoelastic response of one phase to that of a second phase in the material. On the other hand polymeric materials which are essentially homogeneous at the segmental level (homopolymers, random copolymers, and homogenous blocks and blends) are thermorheologically simple (25) materials to which concepts of time-temperature superposition can be readily applied.

In the present case, all of our dynamic mechanical data could be reduced successfully into master curves using conventional shifting procedures. As an example, Figure 7 shows storage and loss modulus master curves and demonstrates the good superposition obtained. In all cases, the shifting was not carried out empirically in order to obtain the best possible superposition; instead the appropriate shift factors were calculated from the WLF equation (26)

$$\log a_T = -\frac{C_1(T-T_o)}{C_2+T-T_o} \tag{2}$$

using C_1 and C_2 values which were weighted averages of the values reported for the two homopolymers (26). The values of these WLF constants are listed in Table 2.

Figure 8 presents the storage and loss modulus master curves obtained on all five samples of interest. The dashed lines indicate extensions of the master curves using appropriately reduced data from the Rheovibron experiments in tension. Storage modulus data in the rubbery plateau region vary systematically with composition, i.e. the modulus increases with the isoprene content of the materials. The interpretation of the behavior in the flow region (low reduced frequency) is not as straightforeward; in particular both of the homopolymers exhibit very much lower slopes than any of the block copolymers. This is probably a consequence of the relatively broad molecular weight distributions of these materials, introduced during the milling procedure (1,13) used to reduce their molecular weights. Similar overall trends are seen in the loss modulus master curves.

All of the evidence presented above supports the conclusion that the diblock copolymers are essentially homogeneous. On the other hand, the corresponding homopolymers have been shown to be incompatible in essentially all proportions under similar conditions of sample preparation. Thus, if at room temperature the BR and IR can be made compatible by the addition of a single chemical bond, i.e. the one linking the two segments in the diblock copolymer, it is not unreasonable to expect that an upper critical solution temperature for the homopolymers might exist not far above room temperature. The direct determination of this temperature by visual methods (27) was not feasible in the present case due to the nearly equal indices of refraction of BR and IR. As an alternative, the dynamic shear properties of a 50/50 blend of IR and BR were determined in the Mechanical Spectrometer from 30° to 200° C.

Isochronal plots of the storage modulus G' vs. temperature for this blend are shown in Figure 9. A clear discontinuity, which is more pronounced at lower frequencies, is observed for all curves around 80° C. This transition was also accompanied by a noticeable decrease in the slope of each of the isochrones at the higher temperatures. A similar, although more dramatic, drop in modulus was observed (8) near 142° C for a styrene-butadiene-styrene triblock copolymer of rather low molecular weight (7,000-43,000-7,000). It was concluded that above this temperature the polystyrene blocks are compatible with the continuous polybutadiene phase. By analogy, one may then conclude that above 80° C the dispersed IR domains in the BR-IR blend under consideration are disrupted resulting in an essentially homogeneous blend.

As a final point regarding compatibility in BR/IR systems, we
consider the effect of diene microstructure. In all the experiments
described above, microstructure was not a variable (Table 1) with pre-
dominantly 1,4 addition appearing in both polymers. In this case it
is possible that the incompatibility of the homopolymers might arise
                    presence of the
from the ∧methyl group in the isoprene repeat unit and/or from the par-
tial trans 1,4 structure of the polybutadiene. On the other hand, it
is interesting to consider whether changes in microstructure (e.g.
higher vinyl content in the polybutadiene) would make the homopolymers
themselves compatible. In order to answer questions of this type, we
studied the compatibility of the polyisoprene (IR) of Table 1 in
blends with several polybutadienes supplied to us by the Phillips
Petroleum Company. The microstructures and molecular weights of
these polymers are shown in Table 3 along with the corresponding
data for IR and BR taken from Table 1.

Binary blends (50/50 wt%) of different combinations of the poly-
mers of Table 3 were prepared from benzene solution as described above.
Either electron microscopy, measurements of dynamic mechanical proper-
ties or both were used to ascertain the heterogeneity (or homogeneity)
of each blend.

Blends of IR and medium-cis BR have already been discussed in detail
and are clearly heterogeneous systems. The blend of IR and high-trans
BR resulted in a completely opaque, white material which was obviously
heterogeneous. A blend of IR and high-cis BR produced a transparent
film which, nonetheless, appeared heterogeneous in the electron micro-
scope (See Figure 10a). Using the same phase contrasting techniques,
a micrograph of a 50/50 blend of high-vinyl BR and medium-cis BR ex-

hibited two phases, as shown in Figure 10b. On the other hand, micro-graphs of the blend of IR and high vinyl BR did not show any evidence of heterogeneity. The loss tangent curve of the same blend exhibited a single peak at a position which was between the loss peak postions of the homopolymers (-49°Cfor IR, -33° C for high vinyl BR, -42°C for the 50/50 blend). This latter system would then offer one possibility for examining the case in which the homopolymers are compatible as well as the corresponding diblock copolymer.

Acknowledgements

Table 1 Characterization of Polymers

Polymer[f]	Weight Percent Isoprene	Molecular Weight[a]	Percent[b] cis 1,4 trans 1,4, Vinyl	
Diblock 2143 (1/1)	56	250000	B:	45,45,10
			I:	90,- ,-
Diblock 2144 (2/1)	39	264000	B:	45,45,10
			I:	90,- ,-
Diblock 2148 (1/2)	71	270000	B:	45,45,10
			I:	90,- ,-
Polyisoprene[c]	100	133000	92,- ,-	
Polybutadiene[d]	0	120000	45,45,10	

(a) Diblocks - via light scattering; Homopolymers - via intrinsic viscosity (after mastication (1)).

(b) Expected microstructure based on anionic polymerization conditions used in the synthesis (See Figure 1 for verification of matched microstructures in the homopolymers and block segments).

(c) Cariflex 309, Shell Nederland Chemie, unmasticated molecular weight 1.5×10^6.

(d) Solprene 233, Phillips Petroleum, unmasticated molecular weight 160,000.

(f) The numbers in parenthesis after each copolymer designation indicate the ratio: moles of butadiene repeat units/moles of isoprene repeat units.

Table 2

WLF Equation Parameters at 0° C

	c_1^o	c_2^o
IR[+]	7.10	127
COP 2148[*] (1/2)	6.26	137
COP 2143[*] (1/1)	5.82	142
COP 2144[*] (2/1)	5.32	148
BR[+]	4.19	162

[+]Adjusted to 0° C from Ref. 26

[*]Weighed averages based on composition (wt%) of the diblock

Table 3

Microstructure and Molecular Weights of

Butadiene and Isoprene Polymers

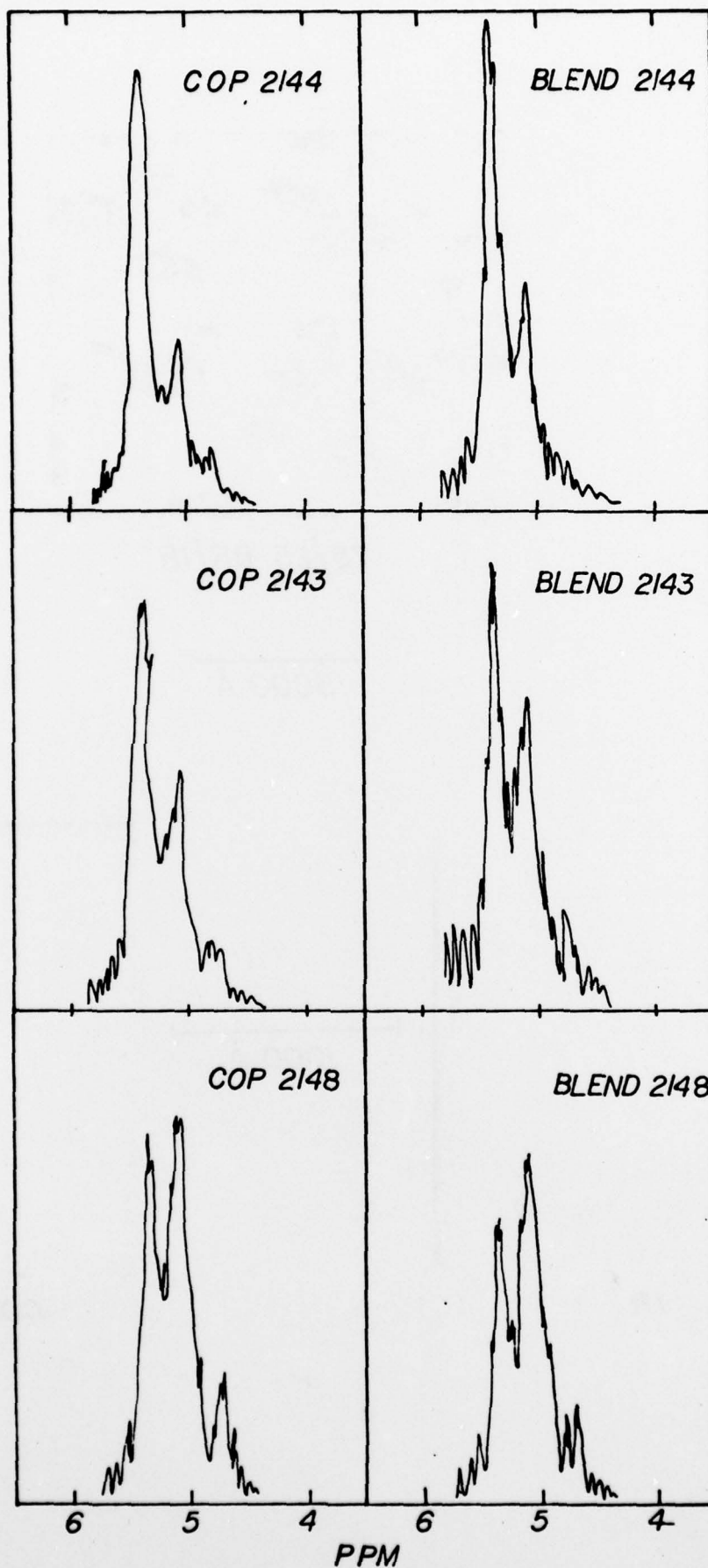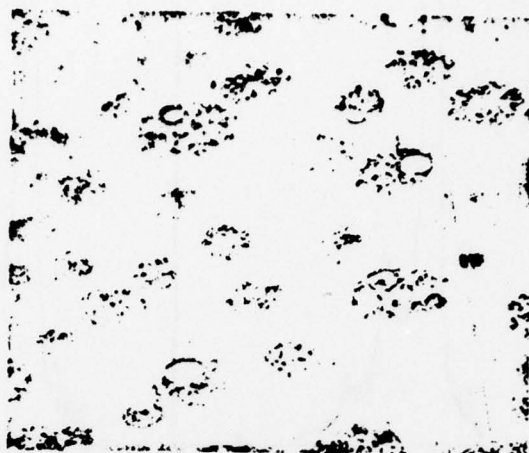|	trans %	cis %	vinyl %	$\overline{M}_w$
High cis BR	4.2	92.0	3.8	416000
Medium cis BR*	45.0	45.0	10.0	120000
High vinyl BR	15.9	19.7	64.4	468000
High trans BR	90.7	-	2.6	156000
High cis IR*	-	92.0	-	133000

*Homopolymers used throughout this work

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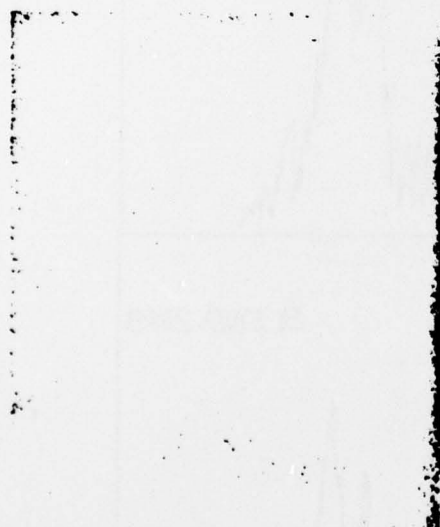
Figure Legends

(1) NMR dpectra of diblock copolymers and corresponding homo-
polymer blends. Spectra obtained in carbontetrachloride
solution with tetramethylsilane internal reference.

(2) Transmission electron micrographs of (a) a blend of poly-
butadiene (25wt%) and polyisoprene (75wt%); (b) polyisoprene
homopolymer; (c) diblock copolymer 2143. Magnifications as
indicated.

(3) Glass transition temperature plotted as a function of isoprene
content for BR-IR homopolymers and diblocks; TMA, 5°C/min.

(4) Tan δ vs. temperature curves at 3.5 Hz for the diblocks and
homopolymers. The scale on the ordinate corresponds to the
bottom curve only, the other curves have been shifted up-
wards for clarity. The two arrows along the temperature
scale indicate the polybutadiene (-82° C) and polyisoprene
(-49° C) transitions.

(5) Location of tan δ peak as a function of composition for BR-
IR homopolymers and diblocks; Rheovibron, 3.5Hz.

(6) Storage modulus isotherms for copolymer 2148(1/2).

(7) Storage and loss modulus master curves for copolymer 2148(1/2)
reduced to 0° C according to the WLF constants shown in Table 2.

(8) Master curves for all five samples listed in Table 1.

(9) Storage modulus isochrones for a 50/50 (wt%) blend of BR and IR.

(10) Electron micrographs of (a) a 50/50 blend of IR and high cis
polybutadiene and (b) a 50/50 blend of medium cis polybuta-
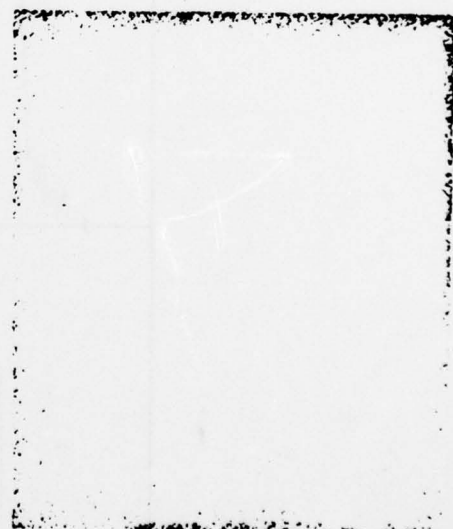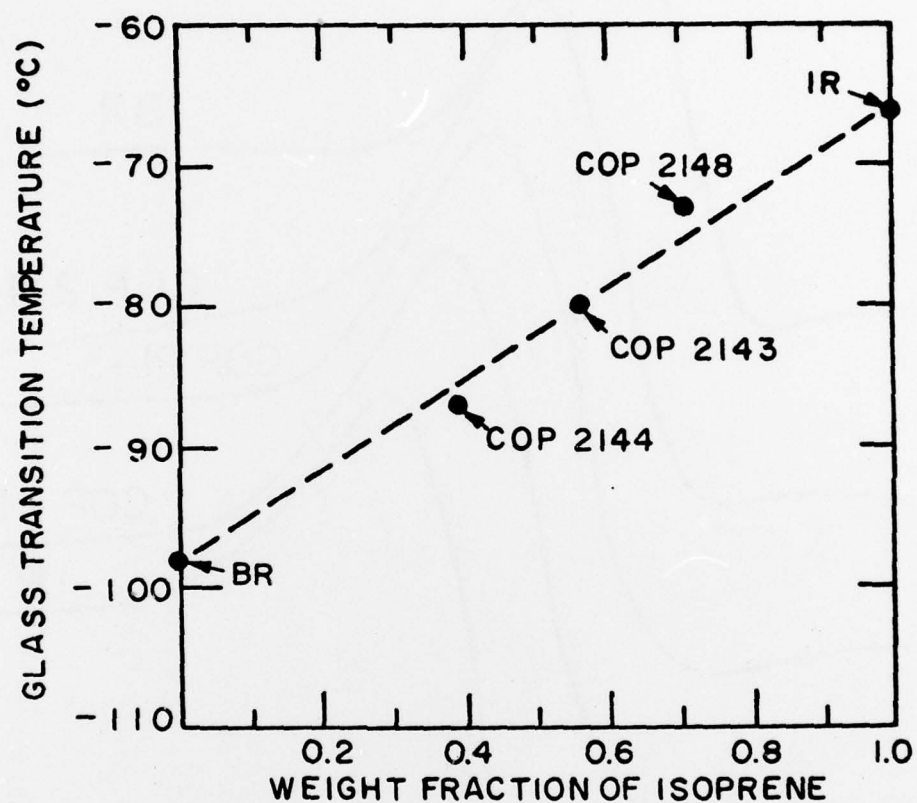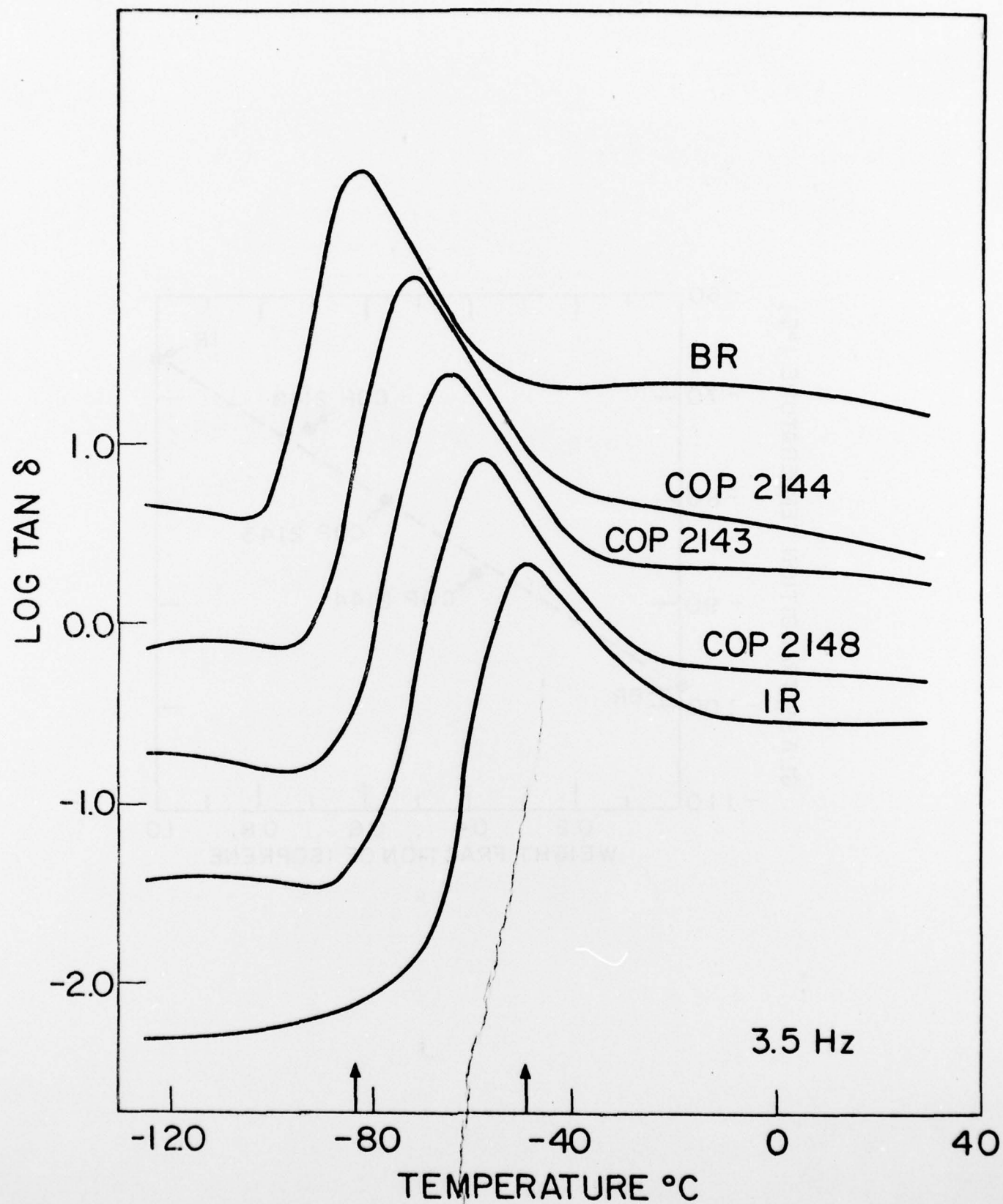diene and high vinyl polybutadiene. See Table 3 for details
of diene microstructures.

COP 2144   BLEND 2144

COP 2143   BLEND 2143

COP 2148   BLEND 2148

PPM

75/25 BR/IR

5000 Å

1000 Å

IR

COP 2143 (1/1)

LOG G' (MPa)

LOG ω (S⁻¹)

Symbol	Temperature
◊	– 29.7 °C
○	– 22.5 °C
○	– 15.0 °C
–	8.2 °C
–	0.9 °C
–	6.7 °C
–	13.7 °C
–	20.7 °C
△	27.4 °C
△	34.7 °C

COP 2148 (29% BR)

COP 2148 (29% BR)
To = 0°C

LOG G', LOG G" (MPa)

LOG ωaᴛ (S⁻¹)

G"

G'

G"

G'

◇ — 29.7°C   ◷ —0.9°C   △ 27.4°C
◇ — 22.5°C   ◷ 6.7°C   △ 34.7°C
◌ — 15.0°C   ◵ 13.7°C
◌ — 8.2°C   ◷ 20.7°C
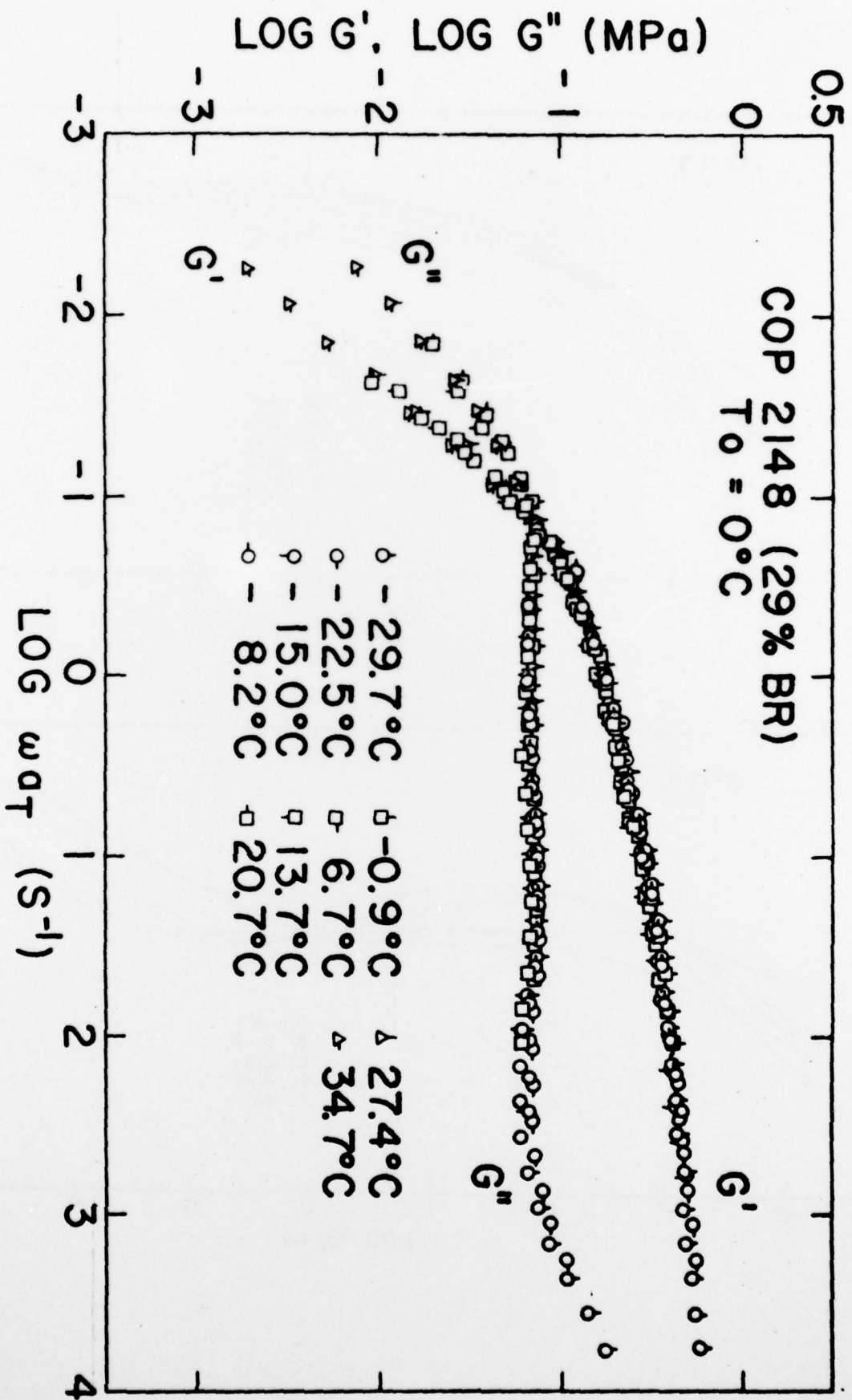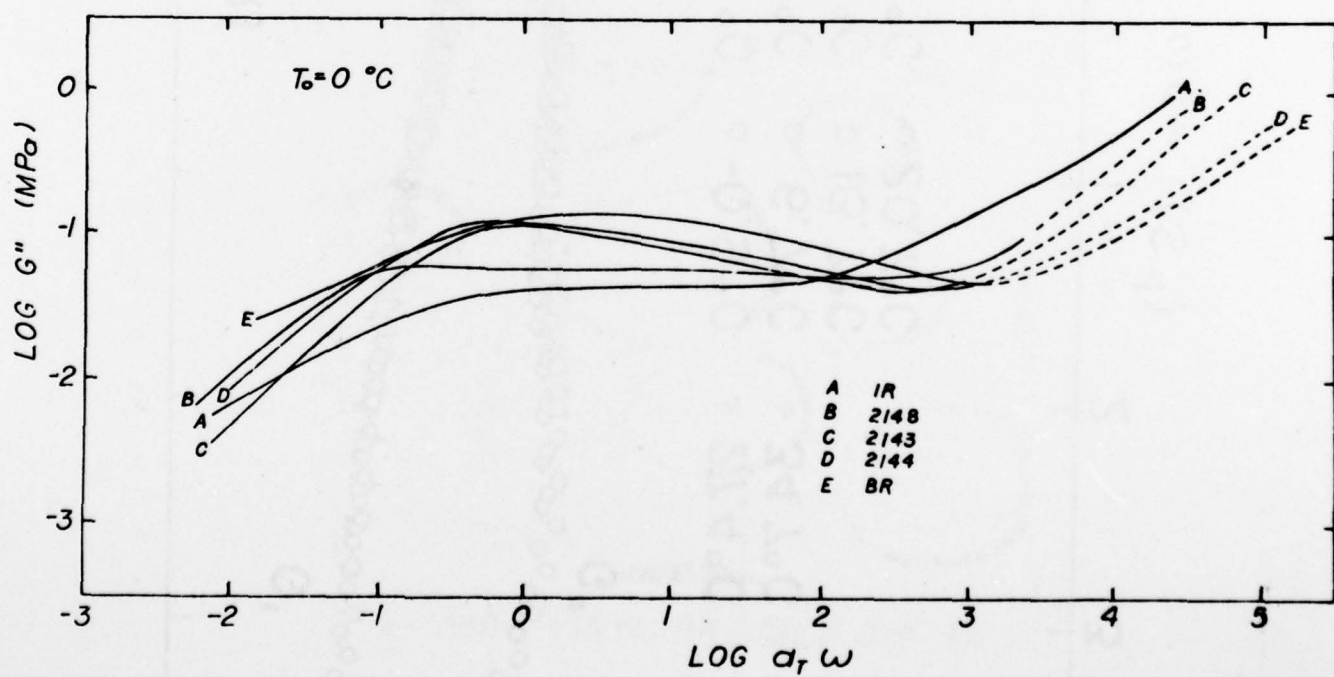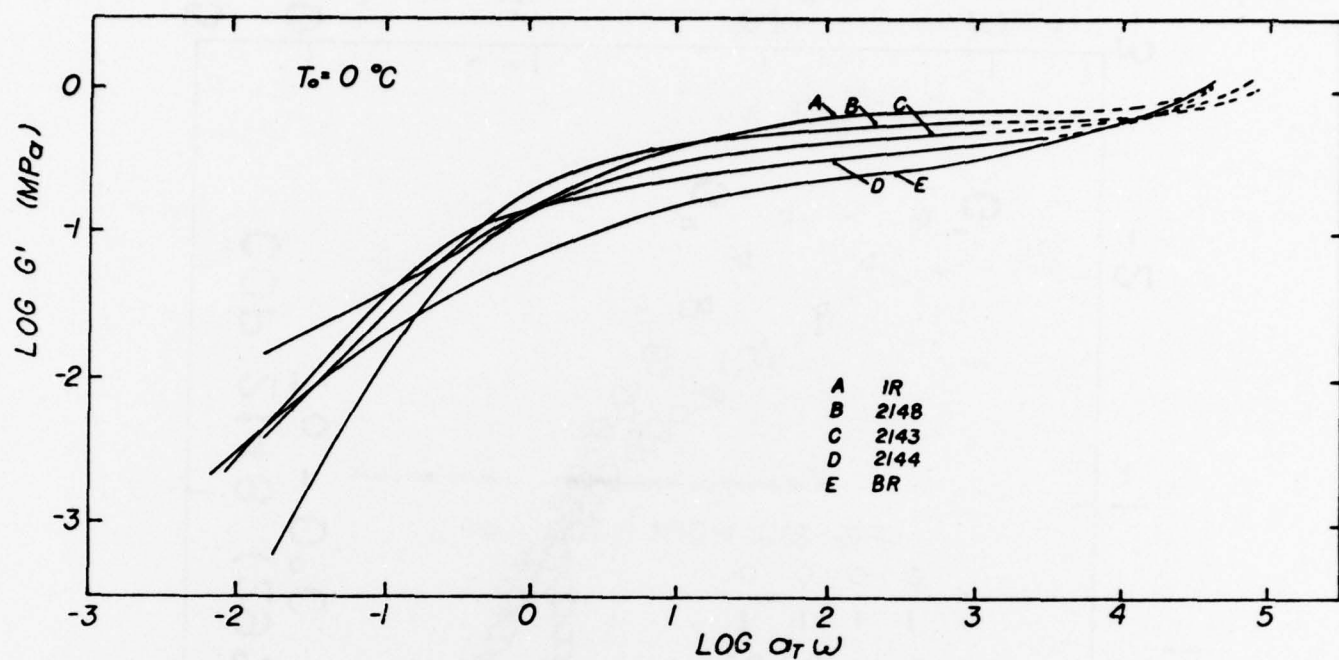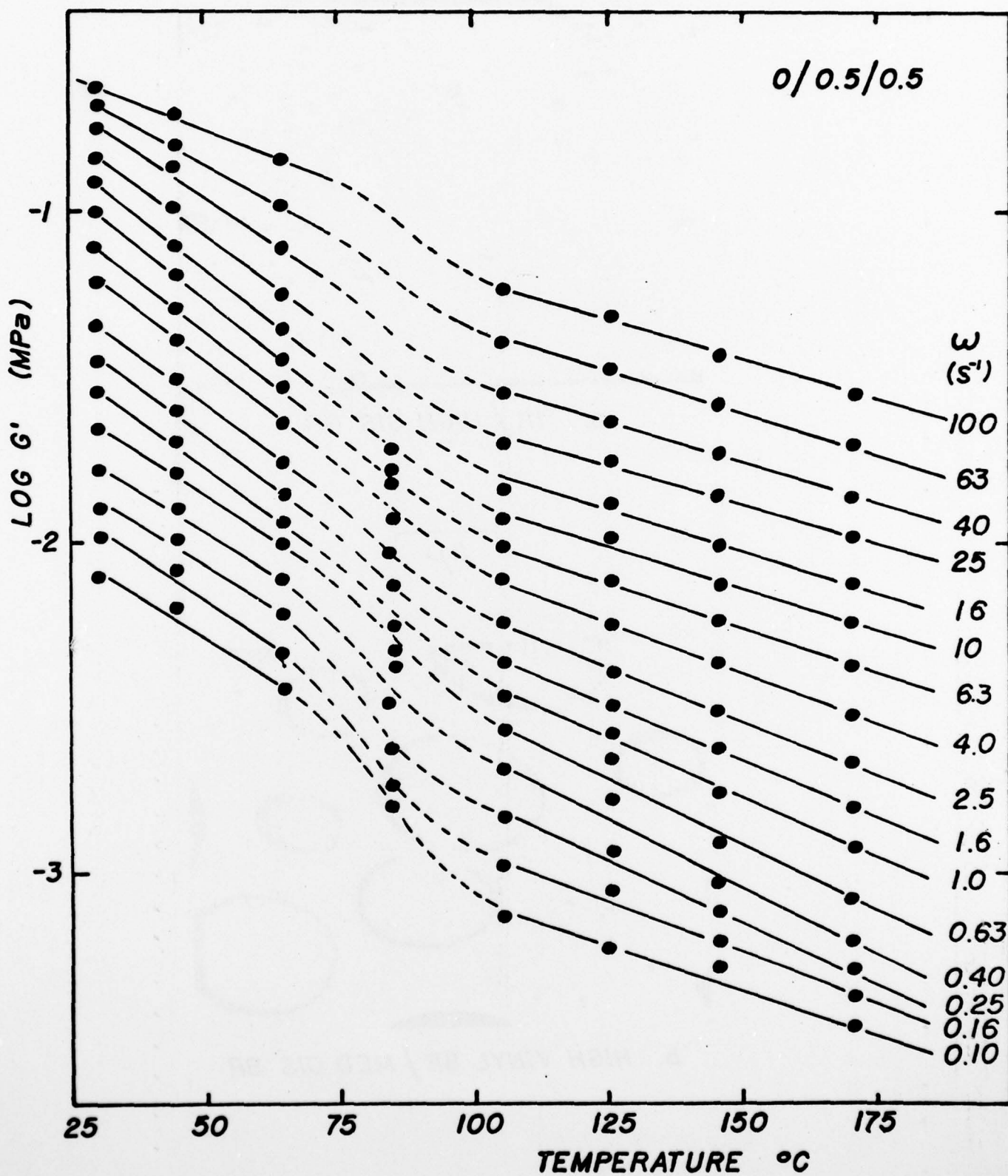
a. IR / HIGH CIS BR

5μ
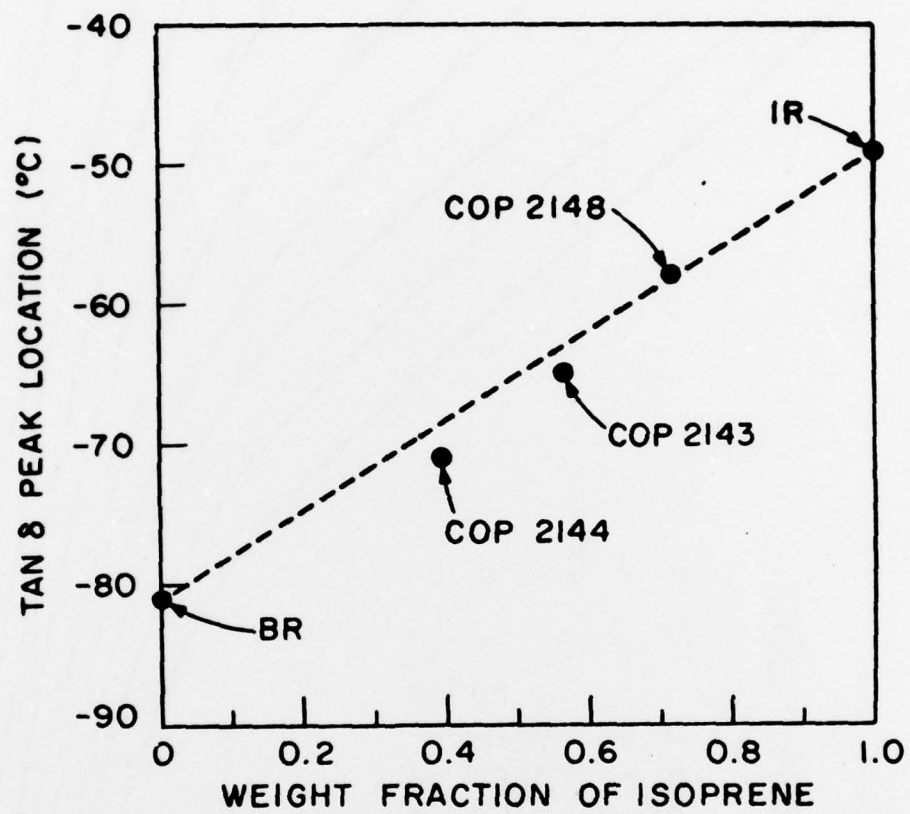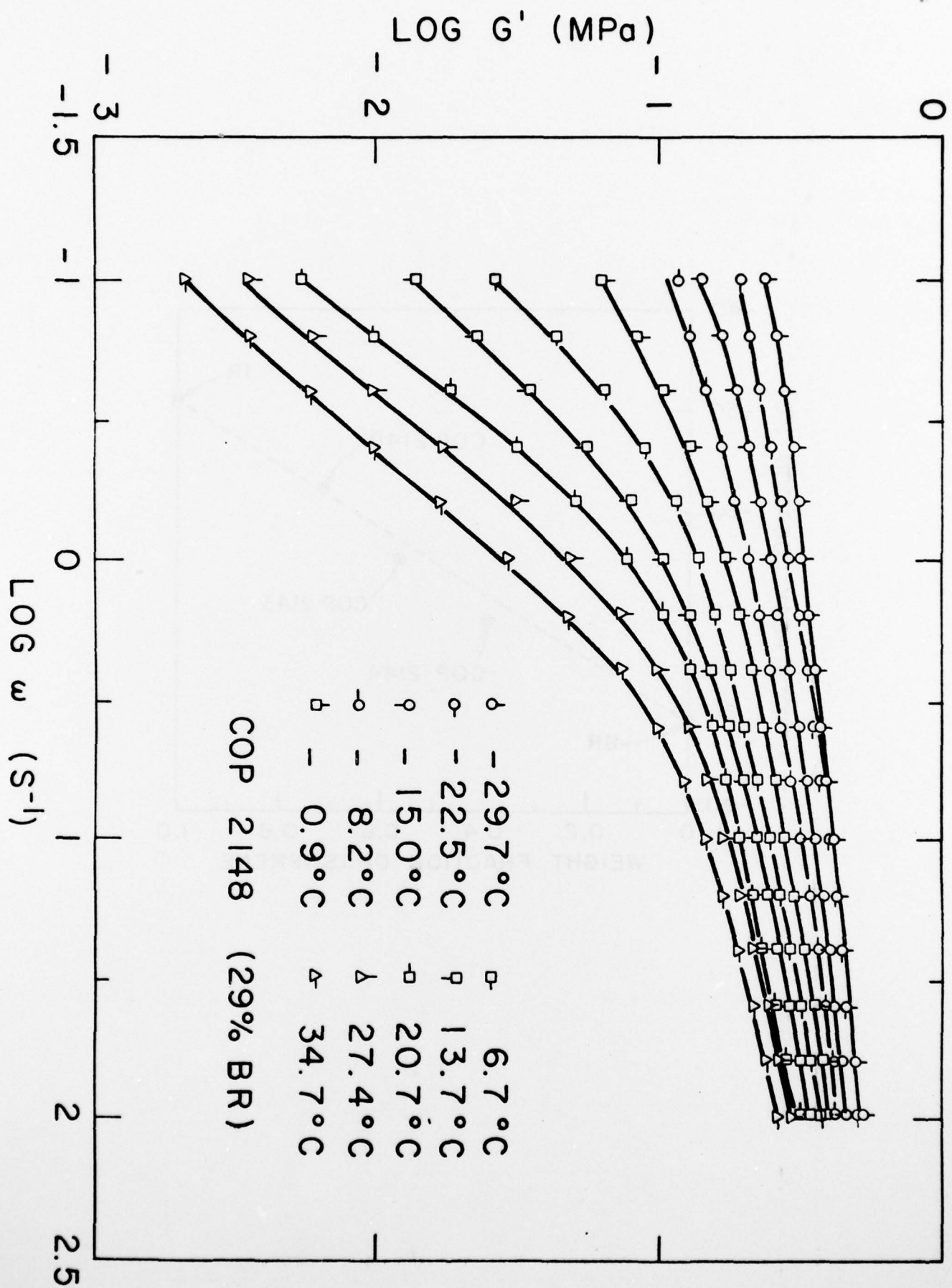
b. HIGH VINYL BR / MED CIS BR

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